

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

| | | |
|--|--|--|
| Applicant's or agent's file reference SMC 60381/WO | FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small> | |
| International application No. PCT/GB 00/ 03113 | International filing date (day/month/year) 14/08/2000 | (Earliest) Priority Date (day/month/year) 16/09/1999 |
| Applicant AVECIA LIMITED | | |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 5 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☒ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

DISAZO DYES AND INKS CONTAINING THEM

5. With regard to the **abstract**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. _____

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 00/03113

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-18 (all partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

On the first line it should be read "chromophore" instead of "chromaphore"

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-18 (all partially)

Present claims 1-11 relate to an extremely large number of possible compounds. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to disazo dyes of the type B--->D--->E prepared by diazotising and coupling from a coupling component "E" containing directive hydroxyl and amino groups, which dyes carry a substituent A-CO-NH-SO₂- attached to the moiety "B", e.g. those compounds prepared in the examples and closely related homologous compounds, as mentioned in the description at page 2, lines 25,26 in combination with the precised definition of the different optional substituents.

Present claim 12 relates to a compound defined by reference to the following parameter: pK_a of the -NH-group. The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the compounds as defined above.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 00/03113

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B31/08 C09D11/02 //B41J2/175

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | FR 2 367 856 A (ACNA) 12 May 1978 (1978-05-12) page 7, line 4 - line 21; examples 29,30 | 1-18 |
| A | US 4 626 284 A (KOBAYASHI MASATSUNE ET AL) 2 December 1986 (1986-12-02) table II, dyes 16,18,22,23; claims | 1-18 |
| A | US 5 198 022 A (AULICK RODNEY O ET AL) 30 March 1993 (1993-03-30) claims; examples | 1-18 |

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 November 2000

Date of mailing of the international search report

15. 11. 00

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ginoux, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/03113

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| FR 2367856 A | 12-05-1978 | IT 1078772 B BE 858524 A BR 7705929 A DE 2739769 A ES 462181 A FR 2372869 A FR 2372868 A JP 53103078 A NL 7709679 A | 08-05-1985 08-03-1978 04-07-1978 16-03-1978 16-06-1978 30-06-1978 30-06-1978 07-09-1978 10-03-1978 |
| US 4626284 A | 02-12-1986 | JP 1763008 C JP 4052306 B JP 60081265 A JP 1594566 C JP 2018711 B JP 60108481 A DE 3436891 A GB 2151250 A,B | 28-05-1993 21-08-1992 09-05-1985 27-12-1990 26-04-1990 13-06-1985 25-04-1985 17-07-1985 |
| US 5198022 A | 30-03-1993 | DE 69224031 D DE 69224031 T EP 0539178 A JP 5262998 A | 19-02-1998 02-07-1998 28-04-1993 12-10-1993 |

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) SMC 60381/WO

| | |
|--|---|
| Box No. I TITLE OF INVENTION Compound | |
| Box No. II APPLICANT | |
| Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) Avecia Limited Hexagon House Blackley Manchester M9 8ZS United Kingdom | <input type="checkbox"/> This person is also inventor. Telephone No. 0161 740 1460 Facsimile No. 0161 721 5801 Teleprinter No. |
| State (that is, country) of nationality: GB | State (that is, country) of residence: GB |
| This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box | |
| Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S) | |
| Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) JAMES, Mark Robert Hexagon House PO Box 42 Blackley, Manchester M9 8ZS United Kingdom | This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.) |
| State (that is, country) of nationality: GB | State (that is, country) of residence: GB |
| This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box | |
| <input type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet. | |
| Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE | |
| The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: <input checked="" type="checkbox"/> agent <input type="checkbox"/> common representative | |
| Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) MAYALL, John Intellectual Property Group Avecia Limited PO Box 42, Hexagon House Blackley Manchester M9 8ZS United Kingdom | Telephone No. 0161 721 1794 Facsimile No. 0161 721 5801 Teleprinter No. |
| <input type="checkbox"/> Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent. | |

Box No. V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☒ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|---|---|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LR Liberia |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LS Lesotho |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MA Morocco |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CR Costa Rica | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> DM Dominica | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TZ United Republic of Tanzania |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> ZA South Africa |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> ZW Zimbabwe |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | |
| <input checked="" type="checkbox"/> KR Republic of Korea | |
| <input checked="" type="checkbox"/> KZ Kazakhstan | |
| <input checked="" type="checkbox"/> LC Saint Lucia | |
| <input checked="" type="checkbox"/> LK Sri Lanka | |

~~Continuation in part~~

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

- ☒ **DZ** Algeria ☒ **MZ** Mozambique
- ☒ **AG** Antigua and Barbuda ☒ **BZ** Belize

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Supplemental Box

If the Supplemental Box is not used, this sheet should not be included in the request.

1. If, in any of the Boxes, **the space is insufficient** to furnish all the information: in such case, write "Continuation of Box No. ..." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) **if more than two persons are involved as applicants and/or inventors** and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "**the States indicated in the Supplemental Box**" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, **the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America**: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) if, in addition to the agent(s) indicated in Box No. IV, there are **further agents**: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
- (v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "**patent of addition**," or "**certificate of addition**," or if, in Box No. V, the name of the United States of America is accompanied by an indication "**continuation**" or "**continuation-in-part**": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No. VI, there are **more than three earlier applications whose priority is claimed**: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI;
- (vii) if, in Box No. VI, **the earlier application is an ARIPO application**: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.

2. If, with regard to the **precautionary designation statement** contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.

3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning **non-prejudicial disclosures or exceptions to lack of novelty**: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.

Continuation of Box IV

FAWKES, David Melville
 LOCKE, Timothy John
 NELSON, Michael Andrew
 PUGSLEY, Roger Graham
 REVELL, Christopher
 SCHMITT, Maja
 SELLER, Alan

All of Intellectual Property Group, Avecia Limited, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, United Kingdom


| Box No. VI PRIORITY CLAIM | | <input type="checkbox"/> Further priority claim indicated in the Supplemental Box. | | |
|---|----------------------------------|--|--|--|
| Filing date of earlier application (day/month/year) | Number of earlier application | Where earlier application is: | | |
| | | national application: country | regional application: regional Office | international application: receiving Office |
| item (1) 16/09/1999 16 September 1999 | 9921928.9 | GB | | |
| item (2) | | | | |
| item (3) | | | | |

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 1

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

| | | | |
|---|--|---|--------|
| Box No. VII INTERNATIONAL SEARCHING AUTHORITY | | | |
| Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used): | | Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority): | |
| | | Date (day/month/year) | Number |
| ISA / EPO | | | |

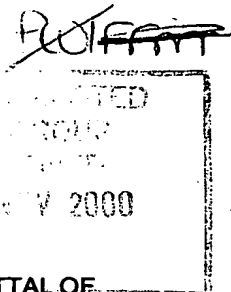
| | |
|--|---|
| Box No. VIII CHECK LIST; LANGUAGE OF FILING | |
| This international application contains the following number of sheets: request : 04 description (excluding sequence listing part) : 14 claims : 02 abstract : 01 drawings : sequence listing part of description : Total number of sheets : 21 | This international application is accompanied by the item(s) marked below: 1. <input checked="" type="checkbox"/> fee calculation sheet 2. <input checked="" type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney, reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input type="checkbox"/> other (specify): |
| Figure of the drawings which should accompany the abstract: | Language of filing of the international application: ENGLISH |

| | |
|--|--|
| Box No. IX SIGNATURE OF APPLICANT OR AGENT | |
| Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request). | |
| For Avecia Limited - JAMES M R  MAYALL, John | |

| | |
|---|--|
| For receiving Office use only | |
| 1. Date of actual receipt of the purported international application: | 2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received: |
| 3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application: | |
| 4. Date of timely receipt of the required corrections under PCT Article 11(2): | |
| 5. International Searching Authority (if two or more are competent): ISA / | 6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid. |

| |
|---|
| For International Bureau use only |
| Date of receipt of the record copy by the International Bureau: |

PATENT COOPERATION TREATY



From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:

Avecia Limited
Intellectual Property Group
Attn. MAYALL, John
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
UNITED KINGDOM

Date of mailing
(day/month/year)

15. 11. 00

Applicant's or agent's file reference

SMC 60381/WO

FOR FURTHER ACTION

See paragraphs 1 and 4 b low

International application No.

PCT/GB 00/ 03113

International filing date
(day/month/year)

14/08/2000

Applicant

AVECIA LIMITED

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Fascimile No.: (41-22) 740.14.35

| DATA ENTERED INTO ZIPIS | DATE | INITIALS |
|-------------------------|----------|----------|
| REMINDED CREATED | 21/11/00 | GT |
| ENTRY TO VERIFY | | |
| ENTRY VERIFIED | | |

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Emmanuel Cherqui

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

TES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

| | |
|---|--|
| Date of mailing (day/month/year) 15 May 2001 (15.05.01) | |
| International application No. PCT/GB00/03113 | Applicant's or agent's file reference SMC 60381/WO |
| International filing date (day/month/year) 14 August 2000 (14.08.00) | Priority date (day/month/year) 16 September 1999 (16.09.99) |
| Applicant JAMES, Mark, Robert | |

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 20 March 2001 (20.03.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

| | |
|---|---|
| The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35 | Authorized officer Olivia TEFY Telephone No.: (41-22) 338.83.38 |
|---|---|

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| | | |
|--|---|--|
| Applicant's or agent's file reference SMC 60381/WO | FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) | |
| International application No. PCT/GB00/03113 | International filing date (<i>day/month/year</i>) 14/08/2000 | Priority date (<i>day/month/year</i>) 16/09/1999 |
| International Patent Classification (IPC) or national classification and IPC C09B31/08 | | |
| Applicant AVECIA LIMITED | | |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 7 sheets, including this cover sheet.

- ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

| | |
|---|--|
| Date of submission of the demand 20/03/2001 | Date of completion of this report 09.11.2001 |
| Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016 | Authorized officer Ginoux, C Telephone No. +31 70 340 2839  |

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

10/088307
JC10 Rec'd PCT/PTO 18 MAR 2002

International application No. PCT/GB00/03113

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-14 as originally filed

Claims, No.:

1-18 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/03113

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- ☐ the entire international application.
- ☒ claims Nos. 1-18 (all partially).

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):
 - ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):
 - ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
 - ☒ no international search report has been established for the said claims Nos. 1-18 (all partially).
2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:
- ☐ the written form has not been furnished or does not comply with the standard.
 - ☐ the computer readable form has not been furnished or does not comply with the standard.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | |
|-------------------------------|------------------|
| Novelty (N) | Yes: Claims 1-18 |
| | No: Claims |
| Inventive step (IS) | Yes: Claims 1-18 |
| | No: Claims |
| Industrial applicability (IA) | Yes: Claims 1-18 |

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/03113

No: Claims

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/03113

Re Item III**Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

The ISA has issued a partial search report under Article 17(2)(a)(ii) PCT because present claims 1-11 relate to an extremely large number of possible compounds. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope has not been possible. Consequently, the search has been carried out for those parts of the claims which appeared to be supported and disclosed, namely those parts relating to disazo dyes of the type B--->D--->E prepared by diazotising and coupling from a coupling component "E" containing directive hydroxyl and amino groups, which dyes carry a substituent A-CO-NH-SO₂- attached to the moiety "B", e.g. those compounds prepared in the examples and closely related homologous compounds, as mentioned in the description at page 2, lines 25,26 in combination with the precised definition of the different optional substituents

Therefore, no International Preliminary Examination has been carried out in respect of subject-matter which has not been covered by the search report (see Rule 66.1() PCT).

Re Item V**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

D1: FR, A, 2 367 856

D2: US, A, 4 626 284

Novelty:

D1 (see examples 29,30) discloses compounds comprising a disazo chromophore and an acyl group linked together through a -SO₂-NH- group. These compounds can be regarded as novelty-destroying for the subject-matter of the application as broadly formulated in claim 1.

However, as indicated above (see Item III), the ISA has issued a partial search report under Article 17(2)(a)(ii) PCT and the search has been carried out for those parts of the claims relating to disazo dyes of the type B--->D--->E prepared by diazotising and coupling from a coupling component "E" containing directive hydroxyl and amino groups, which dyes carry a substituent A-CO-NH-SO₂- attached to the moiety "B" (A being an optionally substituted alkyl or aryl group). Consequently, the above-cited compounds of D1 which do not fall under this definition cannot be regarded as novelty-destroying prior art for the subject-matter of the present application which has been the subject of the search and in this respect the criterion set forth in Article 33(2) PCT can be regarded as satisfied.

Inventive step:

Document D2, which is considered to represent the most relevant state of the art, discloses (cf. especially Table 2, compounds 16,18,22,23) disazo dyes carrying a -SO₂-NH₂, -SO₂-NHCH₃ or NH-CO-CH₃ group, used in ink-jet inks from which the (searched) subject-matter of the present application differs by the presence of a specific group SO₂-NH-CO-A attached to the "B" moiety of the disazo chromophore. The problem to be solved by the present invention may therefore be regarded as the provision of alternative disazo dyes for use in the field of ink-jet printing.

D2 does not contain any indication which could lead a skilled person to replace substituents commonly used in the field by the specific substituent of the compounds disclosed in the present application.

D1 on the other hand is concerned with the dyeing of synthetic polyamide fibers and it does not therefore seem that it would be obvious for a skilled person to combine the teachings of these two documents and to arrive without the exercise of inventive skill to the (searched) subject-matter of the present application. The solution to this problem consisting in providing disazo dyes of the type B--->D--->E prepared by diazotising and coupling from a coupling component "E" containing directive hydroxyl and amino groups, which dyes carry a substituent -SO₂-NH-CO-A (A being an optionally substituted alkyl or aryl group) attached to the moiety "B" is therefore considered as involving an inventive step (Article 33(3) PCT).

Claims 13-18 can be considered as meeting the requirements of the PCT with respect to novelty and inventive step as long as they refer to a composition, process, material, apparatus or method characterised by the use of a compound as defined above.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/03113

Re Item VIII

Certain observations on the international application

Claim 12 relates to a compound mainly defined by reference to the following parameter: pKa of the -NH-group. The use of this parameter in the present context where it seems possible to define the invention in other ways, is considered to lead to a lack of clarity within the meaning of Article 6 PCT since it is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art.

PATENT COOPERATION TREATY

Boiffon

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

MAYALL, John
Avecia Limited
Intellectual Property Group
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
GRANDE BRETAGNE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Rule 71.1)

Date of mailing
(day/month/year) 09.11.2001

Applicant's or agent's file reference
SMC 60381/WO

IMPORTANT NOTIFICATION

International application No.
PCT/GB00/03113

International filing date (day/month/year)
14/08/2000

Priority date (day/month/year)
16/09/1999

Applicant
AVECIA LIMITED

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER


The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

| | | |
|---------------------------|----------|----------|
| DATE ENTERED INTO XEN-PAT | DATE | INITIALS |
| TASK REMINDER | 14/11/01 | GT |
| TO BE VERIFIED | YES | NO |
| XEN-PAT ENTRY VERIFIED | | |

Name and mailing address of the IPEA/

 European Patent Office - P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040 Tx: 31 651 epo nl
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Authorized officer

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(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 March 2001 (22.03.2001)

PCT

(10) International Publication Number
WO 01/19925 A1

- (51) International Patent Classification⁷: C09B 31/08, C09D 11/02, B41J 2/175
- (21) International Application Number: PCT/GB00/03113
- (22) International Filing Date: 14 August 2000 (14.08.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
9921928.9 16 September 1999 (16.09.1999) GB
- (71) Applicant (*for all designated States except US*): AVECIA LIMITED [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): JAMES, Mark, Robert [GB/GB]; Hexagon House, PO Box 42, Blackley, Manchester M9 8ZS (GB).
- (74) Agents: MAYALL, John et al.; Intellectual Property Group, Avecia Limited, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: DISAZO DYES AND INKS CONTAINING THEM

(57) Abstract: A compound comprising a disazo chromophore and an optionally substituted acyl group linked together through a -SO₂-NH- group, inks comprising these compounds, ink jet printer cartridges containing these inks and their use in ink jet printing.

WO 01/19925 A1

DISAZO DYES AND INKS CONTAINING THEM

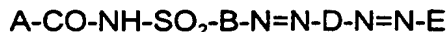
This invention relates to compoundss, to inks comprising these compounds, to ink jet printer cartridges containing these inks and to their use in ink jet printing ("IJP").

IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrat .

5 There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should
10 also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

According to the present invention there is provided a compound comprising a disazo chromophore and an optionally substituted acyl group linked together through a -SO₂NH- group.

15 Preferably where the nitrogen atom of the -SO₂NH- group is attached to the acyl group through a single covalent bond. It is especially preferred that the compound is of Formula (1) and salts thereof:



20 Formula (1)

wherein:

A is an optionally substituted alkyl or aryl group;

B and D are each independently optionally substituted phenylene or naphthylene;

and

25 E is optionally substituted naphthylene.

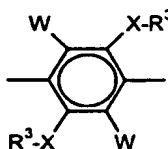
A is preferably an optionally substituted alkyl or aryl group it is especially preferred that A is optionally substituted C₁₋₄-alkyl or optionally substituted phenyl. Preferred optional substituents are selected from; alkoxy, more preferably C₁₋₄-alkoxy; polyalkylene oxide; nitro; cyano; amino; sulpho; halo, especially bromo, chloro or fluoro; ureido; PO₄H₂
30 SO₂F; hydroxy; carboxy; ester, more preferably -CO₂(C₁₋₄-alkyl); and -NR¹R²-COR¹, -CONR¹R² and -SO₂NR¹R² wherein R¹ and R² are each independently H or alkyl, preferably H or C₁₋₄-alkyl .

Preferably B is optionally substituted phenylene, more preferably optionally substituted 1,4-phenylene.

35 Preferred optional substituents which may be present on B, D or E are selected from alkyl, more preferably C₁₋₄-alkyl; alkoxy, more preferably C₁₋₄-alkoxy; polyalkylene oxide; nitro; cyano; amino; sulpho; halo, especially bromo, chloro or fluoro; ureido; PO₄H₂;

SO₂F; hydroxy; carboxy; ester, more preferably -CO₂(C₁₋₄-alkyl); and -NR¹R²-COR¹, -CONR¹R² and -SO₂NR¹R² wherein R¹ and R² are each independently H or alkyl, preferably H or C₁₋₄-alkyl.

Preferably D is an optionally substituted 1,4-phenylene group, more preferably D is of the formula:



wherein each:

W independently is H, optionally substituted alkyl, optionally substituted alkoxy, polyalkylene oxide, nitro, cyano, sulpho, halo, ureido, SO₂F, PO₄H₂, hydroxy, carboxy, ester, -NR¹R², -COR¹, -CONR¹R² or -SO₂NR¹R²;

X independently is O, NH or S;

R¹ and R² are each independently H or alkyl, preferably H or C₁₋₄-alkyl; and

R³ independently is H, optionally substituted alkyl or optionally substituted aryl.

Preferably each W independently is H, C₁₋₄-alkyl or C₁₋₄-alkoxy more preferably H, methyl, ethyl, methoxy or ethoxy, especially H. Preferably both groups represented by W are H and X is O.

Preferably each R³ independently is optionally substituted C₁₋₄-alkyl or optionally substituted phenyl more preferably C₁₋₄-alkyl or C₁₋₄-alkyl-OH, phenyl or phenyl carrying one or two substituents selected from carboxy and sulpho.

When D is also optionally substituted naphthylene it preferably carries one or more (preferably 1 to 4) substituents selected from hydroxy, amino, sulpho and carboxy.

Preferably E is optionally substituted naphthylene, more preferably carrying one or more (preferably from 1 to 4) groups selected from hydroxy, amino, sulpho and carboxy. More preferably E is naphthylene carrying one hydroxy group, one amino group and 0, 1 or 2 sulpho groups. It is especially preferred that E is a 1-hydroxy-3-sulphonaphth-2-ylene group carrying an optionally substituted amino group at the 7-position; or a 1-hydroxy-5-sulphonaphth-2-ylene group carrying an optionally substituted amino group at the 8-position; or a 1-hydroxy-3,6-disulphonaphth-2-ylene group carrying an optionally substituted amino group at the 8-position or a 1-hydroxy-3,6-disulphonaphth-2-ylene group carrying an optionally substituted amino group at the 7-position.

Preferred optionally substituted amino groups are of the formula -NR⁴R⁵ where R⁴ and R⁵ are independently selected from H, optionally substituted alkyl and optionally substituted phenyl. Preferably R⁴ and R⁵ are both H.

The compounds described hereinbefore are preferably soluble in water. To achieve this solubility, the compounds preferably have 1, 2 or 3 water-dispersing

substituents. Preferred water-dispersing substituents are polyalkylene oxides and more preferably sulpho and carboxy.

Preferred polyalkylene oxide groups which may be present on A, B, D and/or E are poly(C₂₋₃-alkylene oxide) groups, more preferably polyethylene glycol or polypropylene glycol, preferably having from 1 to 20 glycol units and terminated with a hydroxy or C₁₋₄-alkoxy group.

Preferably A, B, D and E are selected from the definitions given above such that the pKa of the linking -NH- group (e.g. as shown in Figure 1) is from 8 to 3, more preferably 7.5 to 4, especially 7 to 4.5. These preferences arise from the finding that compounds having such an -NH- group have a particularly good combination of water-fastness and optical density when printed on paper.

Any acid or basic groups on the compound, particularly carboxylic acid and sulphonic acid groups, are preferably in the form of a salt. Thus the Formulae shown herein include the compounds in free acid and in salt form.

The compounds of the invention may be prepared by condensing a diazo chromophore and an optionally substituted acyl compound, where one has a sulphonyl halide substituent and the other has an amino substituent. This condensation is preferably performed in the presence of base to absorb hydrogen halide as it is generated during the condensation.

The compound of Formula A-CO-NH-SO₂-B-N=N-D-N=N-E may be prepared by diazotising an amine of the formula A-CO-NH-SO₂-B-N=N-D-NH₂ and coupling the resultant diazonium salt with a compound of the formula H-E.

The compound of Formula A-CO-NH-SO₂-B-N=N-D-NH₂ may be prepared by diazotising an amine of the formula A-CO-NH-SO₂-B-NH₂ and coupling the resultant diazonium salt with an amine of the formula H-D-NH₂. In some cases it may be necessary for the amino group to carry a protecting group which should be removed on completion of the reaction.

Many compounds of the formula A-CO-NH-SO₂-B-NH₂ are commercially available.

Preferably they may be prepared by condensing an amine of formula B-(NH₂)₂, in which one of the amino groups is protected, with a compound of formula Cl-SO₂-NH-CO-A followed by removal of the protecting group.

More preferably they may be prepared by condensing an amine of formula A-CO-NH₂ with a compound of formula Cl-SO₂-B-NH₂ carrying a protecting group on the amino group of the Cl-SO₂-B-NH₂ compound, followed by removal of the protecting group.

Diazotisation is preferably performed at a temperature below 6°C, more preferably at a temperature in the range -10°C to 5°C. Preferably diazotisation is performed in water, preferably at a pH below 7 for the monoazo intermediate and above pH7 to form compounds of Formula (1). Dilute mineral acid, e.g. HCl or H₂SO₄, may be used to achieve the desired acidic conditions.

In the above processes, A, B, D and E are as hereinbefore defined.

Any acid or basic groups on the compound, particularly carboxylic acid and sulphonic acid groups, are preferably in the form of a salt. Thus the Formulae shown herein include the compounds in free acid and in salt form.

5 Preferred salts are alkali metal salts, especially lithium, sodium and potassium salts, ammonium and substituted ammonium salts. Especially preferred salts are salts with ammonia and volatile amines. The compounds may be converted into a salt using known techniques. For example, an alkali metal salt of a compound may be converted
10 into a salt with ammonia or an amine by dissolving an alkali metal salt of the compound in water, acidifying with a mineral acid and adjusting the pH of the solution to pH 9 to 9.5 with ammonia or the amine and removing the alkali metal cations by dialysis or by treatment with an ion exchange resin.

The compounds may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present claims. The
15 compounds are particularly useful as dyes, especially for ink jet printing compositions.

According to a second aspect of the present invention there is provided a composition comprising a compound according to the first aspect of the invention, preferably of Formula (1) and a liquid medium.

Preferred compositions comprise:

- 20 (a) from 0.01 to 30 parts of a compound according to the first aspect of the invention, preferably of Formula (1); and
(b) from 70 to 99.99 parts of a liquid medium;
wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably
25 from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates which may be used to prepare more dilute inks and
30 reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water.

When the medium comprises a mixture of water and an organic solvent, the weight
35 ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol,

isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and sulfolane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Although not usually necessary, further colorants may be added to the ink to modify the shade and performance properties. Examples of such colorants include C.I.Direct Yellow 86, 132, 142 and 173; C.I.Direct Blue 199, and 307; C.I.Food Black 2; C.I.Direct Black 168 and 195; C.I.Acid Yellow 23; and any of the dyes used in ink jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International. Addition of such further dyes can increase overall solubility leading to less kogation (nozzle blockage) for the resultant ink.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the compound in the liquid medium. Examples of polar solvents include C₁₋₄-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C₁₋₄-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The liquid media may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

It is preferred that a composition according to the second aspect of the invention is an ink or liquid dye concentrate.

A third aspect of the invention provides a process for forming an image on a substrate comprising applying an ink according to the second aspect of the invention thereto by means of an ink jet printer.

The ink used in this process is preferably a composition as defined in the second aspect of the present invention.

The inks preferably have a total concentration of divalent metal ions and trivalent metal ions below 1000 more preferably below 100, especially below 20, more especially below 10 parts per million by weight relative to the total weight of ink. Pure inks of this type may be prepared by using high purity ingredients and/or by purifying the ink after it has been prepared. Suitable purification techniques are well known, e.g. ultrafiltration, reverse osmosis, ion exchange and combinations thereof.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character.

5 A fourth aspect of the present invention provides a paper, an overhead projector slide or a textile material printed with a composition according to the second aspect of the invention, a compound according to the first aspect of the invention or by means of a process according to third aspect of the invention.

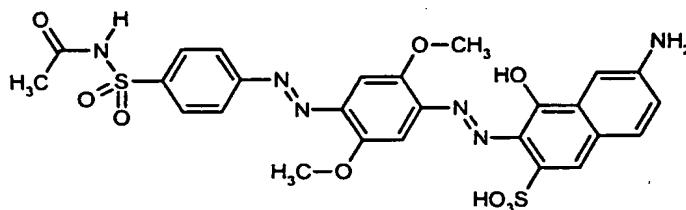
10 A fifth aspect of the present invention provides an ink jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is according to the second aspect of the present invention.

A final aspect of the invention is a method for the colouration of a substrate which comprises treating with a compound according to the first aspect of this invention.

15 The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

Preparation of:



20 Sulfacetamide (16.8 parts) was dissolved in distilled water (550 parts) by the addition of the minimum amount of 47% caustic liquor with stirring. Sodium nitrite (5.68 parts) was then added and the solution was cooled to 0°C. This mixture was poured into pre-cooled (0°C) concentrated hydrochloric acid (75 parts) with vigorous stirring. The mixture was stirred at 0-5°C for 4 hours, then enough sulfamic acid was added to destroy the excess nitrous acid present and the mixture was stirred for a further 15 minutes. This mixture was then added to a stirred mixture of 2,5-dimethoxyaniline (12.6 parts) and methylated spirits (74OP, 400 parts) over approximately 15 minutes with the co-addition of enough ice and saturated sodium acetate solution to maintain the temperature at 0-5°C and the pH in the range of 4-5. The mixture was then stirred at 0-5°C for 1 hour, allowed to warm to room temperature and stirred over night at room temperature. The product was filtered, washed twice with distilled water and dried at approximately 70°C overnight to yield 28.5 parts of product at 91% strength by C, H and N analysis.

25

30

35

The monoazo intermediate (3 parts) and sodium nitrite (0.52 parts) was stirred in distilled water (100 parts) at 0°C. Concentrated hydrochloric acid (7.5 parts) was added with vigorous stirring and the mixture was stirred at 0-5°C for 2 hours. Tetrahydrofuran (150 parts) was added and the mixture was stirred at 0-5°C for a further 3 hours.

5 Sulfamic acid was added to destroy the excess nitrous acid present and the mixture was stirred for a further 15 minutes. This mixture was then added to a stirred solution of gamma acid (1.9 parts) and sodium carbonate (to pH 10-11) in water (100 parts), over approximately 30 minutes with the co-addition of enough ice and 47% caustic liquor solution to maintain the temperature at 0-5°C and the pH in the range of 9.5-10. The
10 mixture was stirred at 0-5°C for 1 hour, allowed to warm to room temperature and stirred overnight at room temperature. The mixture was acidified to pH 3 by the slow addition of concentrated hydrochloric acid, the product was filtered, washed with dilute hydrochloric acid and triturated twice with acetone (170 parts) containing 880 ammonia (3 drops).

The crude sodium salt was then exchanged for the ammonium salt by dissolving
15 the compound in aqueous ammonia at approximately pH 10-11 and slowly pouring this solution into an equal volume of vigorously stirred 2N hydrochloric acid. The precipitated compound was filtered and the ion exchange process repeated.

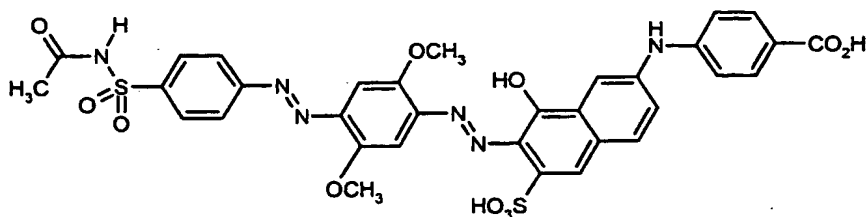
The crude ammonium salt was dissolved in dilute aqueous ammonia at approximately pH 10-11, filtered through a GF-A and GF-F glass fibre filter and dialysed
20 using 'Visking tubing'. This solution was dried at approximately 70°C overnight to yield 1.8 parts of product which shown to have the correct structure by nmr and mass spectral analysis.

Inks were then prepared by dissolving the specified % of the compound in a stock solution of 9 parts water and 1 part 1-methyl-2-pyrrolidinone with the addition of
25 concentrated ammonia to give a pH of 9-10. The inks were then filtered through a 0.45 micron membrane filter and printed using HP 560 thermal IJ printer. The following results were obtained on Wiggins Conquer paper:

| | % Dye in ink | OD | Run down (24 h) |
|----|--------------|-------|-----------------|
| 30 | 2.5 | 1.446 | 4 |

* OD means optional density of the printed paper, as measured by an x-rite spectrometer.

Rundown was measured by printing the ink in parallel bands onto the paper, allowing the printed paper to dry for 24 hours, placing the printed paper at an angle of 45°
35 and pouring 0.25ml of water down the paper. The run down (a measure of wet-fastness) was given a score of 1 to 10, where 10 means no visible ink run (high wet-fastness).

Example 2Preparation of:

5 Example 1 was repeated except that p-carboxyphenyl gamma acid was used in place of gamma acid in the final coupling reaction.

Inks containing the title dye were prepared and printed onto Gilbert Bond paper (as NH_4^+ salt) as described in Example 1.

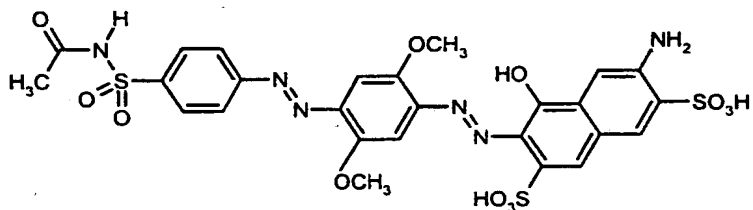
The following results were obtained:

10

| % Dye in ink | OD | Run down (24 h) |
|--------------|-------|-----------------|
| 2.5 | 1.113 | 9 |

Example 3

15

Preparation of:

Example 1 was repeated except that 2-R acid was used in place of gamma acid in the final coupling reaction.

20

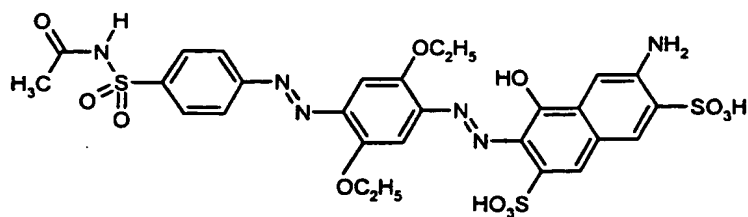
Inks containing the title dye were prepared as in Example 1 except a mixture of glycerol (10%), butyldiglycol (10%), and surfynol 465 (1%) was used in place of N-methyl-2-pyrrolidone and the resultant ink was printed onto Xerox Acid (as NH_4^+ salt) paper using a Epson Color 660 printer.

The following results were obtained:

25

| % Dye in ink | OD |
|--------------|-------|
| 6% | 1.299 |

30

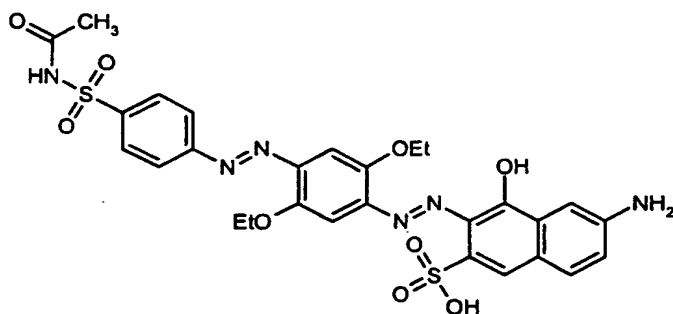
Example 4**Preparation of:**

Example 1 was repeated except that 2,5-diethoxyaniline was used in place of that 2,5-dimethoxyaniline in the first coupling reaction and 2-R acid was used in place of gamma acid in the final coupling..

Inks containing the title dye were prepared as in Example 1 except a mixture of glycerol (7.5%), thiodiglycol (7.5%), urea (7.5%) and surfynol 465 (1%) was used in place of N-methyl-2-pyrrolidone and the resultant ink was printed onto Xerox Acid (as NH₄⁺ salt) paper using a Canon BJC-2000 printer.

The following results were obtained:

| % Dye in ink | OD | Run down (24 h) |
|--------------|-------|-----------------|
| 3.5 | 1.075 | 8.5 |

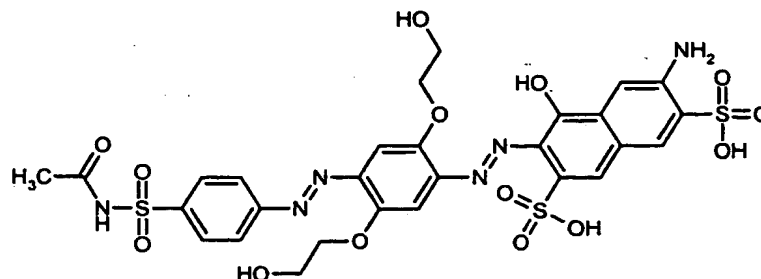
Example 5**Preparation of:**

Example 1 was repeated except 2,5-diethoxyaniline was used in place of 2,5-dimethoxyaniline in the first coupling reaction.

Inks containing the title dye were prepared and printed onto Xerox Acid paper as described in Example 1.

The following results were obtained:

| % Dye in ink | OD | Run down (24 h) |
|--------------|------|-----------------|
| 2.5% | 1.01 | 7 |

Example 6Preparation of:

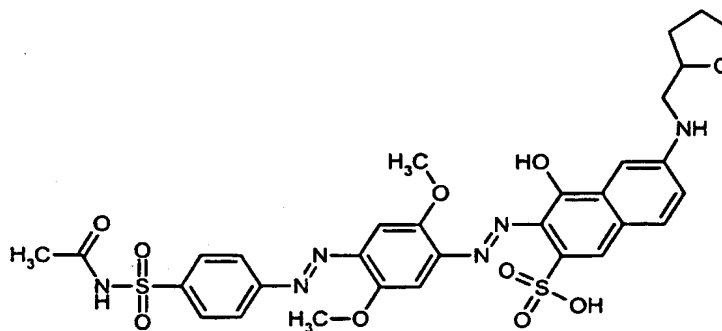
5

Example 1 was repeated except 2,5-di(2-hydroxyethoxy)aniline replaced 2,5-dimethoxyaniline in the first coupling reaction and 2-R acid was used in place of gamma acid in the final coupling.

Inks containing the title dye were prepared as described in Example 5 of PCT/GB00/02280 and printed onto Xerox Acid (as Na⁺ salt) paper as described in Example 1.

The following results were obtained:

| | % Dye in ink | OD | Run down (24 h) |
|----|--------------|------|-----------------|
| 15 | 3 | 1.07 | 7.5 |

Example 7Preparation of:

20

Example 1 was repeated except tetrahydrofurfuryl gamma acid was used in place of gamma acid in the final coupling. Tetrahydrofurfuryl gamma acid was prepared as described in Example 1, stage 2 of WO 9732931 except that tetrahydrofurfurylamine replaced (2-aminoethyl)piperazine.

25

Inks containing the title dye were prepared as described in Example 5 of PCT/GB00/02280 and printed onto Xerox Acid (as Na⁺ salt) paper as described in Example 1.

The following results were obtained:

| % Dye in ink | OD | Run down (24 h) |
|--------------|------|-----------------|
| 3 | 1.08 | 8 |

5

Further Inks

The inks described in Tables I and II may be prepared wherein the Dye described in the first column is the Dye made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

10

The following abbreviations are used in Table I and II:

PG = propylene glycol

DEG = diethylene glycol

15

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

20

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET = cetyl ammonium bromide

PHO = Na_2HPO_4 and

25

TBT = tertiary butanol

TDG = thiodiglycol

TABLE I

| Example | Dye Content | Water | PG | DEG | NMP | DMK | NaOH | Na Stearate | IPA | MEOH | 2P | MIBK |
|---------|-------------|-------|----|-----|-----|-----|------|-------------|-----|------|----|------|
| 1 | 2.0 | 80 | 5 | | 6 | 4 | | | | | 5 | |
| 2 | 3.0 | 90 | | 5 | 5 | | 0.2 | | | | | |
| 3 | 10.0 | 85 | 3 | | 3 | 3 | | | | 5 | 1 | |
| 4 | 2.1 | 91 | | 8 | | | | | | | | 1 |
| 5 | 3.1 | 86 | 5 | | | | | 0.2 | 4 | | | 5 |
| 6 | 1.1 | 81 | | | 9 | | 0.5 | | | | 9 | |
| 7 | 2.5 | 60 | 4 | 15 | 3 | 3 | | | 6 | 10 | 5 | 4 |
| 1 | 5 | 65 | | 20 | | | | | 10 | | | |
| 3 | 2.4 | 75 | 5 | 4 | | 5 | | | | 6 | | 5 |
| 4 | 4.1 | 80 | 3 | 5 | 2 | 10 | | 0.3 | | | | |
| 1 | 3.2 | 65 | | 5 | 4 | 6 | | | 5 | 4 | 6 | 5 |
| 6 | 5.1 | 96 | | | | | | | | 4 | | |
| 2 | 10.8 | 90 | 5 | | | | | | 5 | | | |
| 5 | 10.0 | 80 | 2 | 6 | 2 | 5 | | | 1 | | 4 | |
| 1 | 1.8 | 80 | | 5 | | | | | | | 15 | |
| 1 | 2.6 | 84 | | | 11 | | | | | | 5 | |
| 1 | 3.3 | 80 | 2 | | | 10 | | | | 2 | | 6 |
| 1 | 12.0 | 90 | | | | 7 | 0.3 | | 3 | | | |
| 1 | 5.4 | 69 | 2 | 20 | 2 | 1 | | | | | 3 | 3 |
| 1 | 6.0 | 91 | | | 4 | | | | | | 5 | |

TABLE II

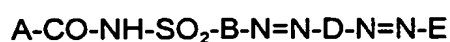
| Example | Dye Content | Water | PG | DEG | NMP | CET | TBT | TDG | BDL | PHO | 2P | PI2 |
|---------|----------------|-------|----|-----|-----|------|-----|-----|-----|------|----|-----|
| 1 | 3.0 | 80 | 15 | | | 0.2 | | | | | 5 | |
| 2 | 9.0 | 90 | | 5 | | | | | | 1.2 | 5 | |
| 3 | 1.5 | 85 | 5 | 5 | | 0.15 | 5.0 | 0.2 | | 0.12 | | |
| 4 | 2.5 | 90 | | 6 | 4 | | | | | | | |
| 5 | 3.1 | 82 | 4 | 8 | | 0.3 | | | | | 6 | |
| 6 | 0.9 | 85 | | 10 | | | | | 5 | 0.2 | | |
| 7 | 8.0 | 90 | | 5 | 5 | | | 0.3 | | | | |
| 1 | 4.0 | 70 | | 10 | 4 | | | | 1 | | 4 | 11 |
| 2 | 2.2 | 75 | 4 | 10 | 3 | | | | 2 | | 6 | |
| 3 | 10.0 | 91 | | | 6 | | | | | | 3 | |
| 4 | 9.0 | 76 | | 9 | 7 | | 3.0 | | | 0.95 | 5 | |
| 5 | 5.0 | 78 | 5 | 11 | | | | | | | 6 | |
| 7 | 5.4 | 86 | | | 7 | | | | | | 7 | |
| 1 | 2.1 | 70 | 5 | 5 | 5 | 0.1 | 0.2 | 0.1 | 5 | 0.1 | 5 | |
| 1 | 2.0 | 90 | | 10 | | | | | | | | |
| 1 | 2 | 88 | | | | | | 10 | | | | |
| 1 | 5 | 78 | | | 5 | | | 12 | | | 5 | |
| 6 | 8 | 70 | 2 | | 8 | | | 15 | | | 5 | |
| 1 | 10 | 80 | | | | | | 8 | | | 12 | |
| 1 | 10 | 80 | | 10 | | | | | | | | |

CLAIMS

1. A compound comprising a disazo chromophore and an optionally substituted acyl group linked together through a -SO₂-NH- group.

2. A compound according to claim 1 wherein the nitrogen atom of the -SO₂-NH- group is attached to the acyl group through a single covalent bond.

3. A compound according to any one of the preceding claims of Formula (1) and salts thereof:



Formula (1)

wherein:

A is an optionally substituted alkyl or aryl group;

B and D are each independently optionally substituted phenylene or naphthylene;

and

E is optionally substituted naphthylene.

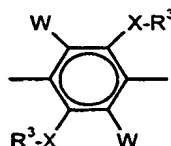
4. A compound according to any one of the preceding claims wherein A is optionally substituted C₁₋₄-alkyl or optionally substituted phenyl.

5. A compound according to any one of claim 3 or claim 4 wherein B is optionally substituted phenylene.

6. A compound according to any one of claims 3 to 5 wherein B is optionally substituted 1,4- phenylene.

7. A compound according to any one of claims 3 to 5 wherein D is optionally substituted 1,4- phenylene.

8. A compound according to any one of claims 3 to 6 wherein D is of the formula:



wherein each:

W independently is H, C₁₋₄-alkyl, alkoxy, polyalkylene oxide, nitro, cyano, amino, sulpho, halo, ureido, SO₂F, PO₄H₂, hydroxy, carboxy, ester, -NR¹R², -COR¹, -CONR¹R² or -SO₂NR¹R², wherein R¹ and R² are each independently H or alkyl;

X independently is O, NH or S;

R³ independently is H or optionally substituted alkyl or optionally substituted aryl.

5 9. A compound according to any one of claims 3 to 6 wherein D is naphthylene carrying one or more groups selected from hydroxy, amino, sulpho and carboxy.

10 10. A compound according to any one of claims 3 to 9 wherein E is naphthylene carrying one or more substituents selected from hydroxy, amino, sulpho and carboxy.

11. A compound according to any one of claims 3 to 11 wherein E is a 1-hydroxy-3-sulphonaphth-2-ylene group carrying an optionally substituted amino group at the 7-position; or a 1-hydroxy-5-sulphonaphth-2-ylene group carrying an optionally substituted amino group at the 8-position; or a 1-hydroxy-3,6-disulphonaphth-2-ylene group carrying an optionally substituted amino group at the 8-position or a 1-hydroxy-3,6-disulphonaphth-2-ylene group carrying an optionally substituted amino group at the 7-position

12. A compound according to any one of the preceding claims wherein the pKa of the -NH- group is from 8 to 3.

13. A composition comprising a compound according to any one of claims 1 to 12 and a liquid medium.

14. A composition according to claim 13 which is an ink or liquid dye concentrate.

15. A process for forming an image on a substrate comprising applying an ink according to claim 14 thereto by means of an ink jet printer.

16. A paper, an overhead projector slide or a textile material printed with an ink according to claim 14, with a compound according to any one of claims 1 to 12 or by means of a process according to claim 15.

17. An ink jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is according to claim 14.

18. A method for the colouration of a substrate which comprises treating with a compound according to any one of claims 1 to 12.